

Borosilicate glass of high chemicals resistance, and
its uses

The invention relates to a borosilicate glass of high
5 chemicals resistance and to its uses.

Fused glass/metal seals which are used in a chemically
corrosive environment, for example in the construction
of chemical installations or reactors, require glasses
10 which have a very high resistance to both acidic and
basic media. Moreover, the thermal expansion of sealing
glasses of this type has to be matched to the
chemically highly resistant metals or alloys which are
used. In this context, it is desirable for the
15 coefficient of linear thermal expansion to be close to
or slightly below that of the metal which is to be
sealed, so that during cooling of the fused seal,
compressive stresses are built up in the glass, these
stresses first ensuring a hermetic seal and secondly
20 preventing tensile stresses from building up in the
glass, which would promote the occurrence of stress
crack corrosion. When using Fe-Ni-Co alloys, e.g.
Vacon® 11, with a coefficient of thermal expansion
25 $\alpha_{20/300}$ of $5.4 \times 10^{-6}/\text{K}$, or zirconium ($\alpha_{20/300} = 5.9 \times 10^{-6}/\text{K}$) or zirconium alloys, glasses with an expansion
coefficient $\alpha_{20/300}$ of between > 5 and $6.0 \times 10^{-6}/\text{K}$ are
required as sealing glasses for fused glass/metal
seals.

30 A crucial parameter for characterizing the workability
of a glass is the working point V_A at which the
viscosity of the glass is 10^4 dPas . It should be low,
since even slight reductions in V_A lead to a
considerable fall in production costs, since the
35 melting temperatures can be reduced. Furthermore, a V_A
which is as low as possible is also advantageous in the
production of the fused glass/metal seal, since it is
then possible to avoid overheating the parts which are

to be fused together, since fusion can occur either at a lower temperature or within a shorter time. Finally, when using glasses with a relatively low V_A it is possible to prevent the seal being adversely affected
5 and, in the most extreme circumstances, leaking as a result of evaporation and recondensation of glass components. Furthermore, the working interval of a glass, i.e. the temperature difference between the working temperature V_A and the softening point E_w , the
10 temperature at which the viscosity of the glass is $10^{7.6}$ dPas, is also of significance. The temperature range within which a glass can be worked is also known as the "length" of the glass.
15 Applications as primary packaging material for pharmaceuticals, such as ampoules or small bottles, also require glasses which have a very high chemical resistance with respect to acidic and basic media and, in particular, a very high hydrolytic stability.
20 Furthermore, a low coefficient of thermal expansion is advantageous, since this ensures a good thermal stability.

Furthermore, the physical-chemical behavior of the
25 glass during its further processing is of importance, since this has an influence on the properties of the end product and on its possible applications.

If a preform made from borosilicate glass which
30 contains alkali metals, e.g. a tube, is processed further under hot conditions to form containers such as ampoules or small bottles, highly volatile alkali metal borates evaporate. The evaporation products condense in cooler regions, i.e. deposits are formed on the
35 vessels, which have an adverse effect on their hydrolytic stability. Therefore, this phenomenon is disadvantageous in particular for applications of the glass in the pharmaceuticals sector, for example as

primary packaging material for pharmaceuticals.

The patent literature has already described glasses which have high chemicals resistances but are in need of improvement in particular with regard to their hydrolytic stability and/or have excessively high working points and/or do not have the desired expansion coefficients.

DE 42 30 607 C1 proposes chemically highly resistant borosilicate glasses which can be fused to tungsten. They have expansion coefficients $\alpha_{20/300}$ of at most $4.5 \times 10^{-6}/K$ and, according to the examples, working points of $\geq 1210^\circ C$.

The borosilicate glasses described in the publication DE 37 22 130 A1 also have a low expansion of at most $5.0 \times 10^{-6}/K$.

The glasses described in patent DE 44 30 710 C1 have a relatively high SiO_2 content, namely $> 75\%$ by weight and $> 83\%$ by weight of $SiO_2 + B_2O_3$ in combination with an SiO_2/B_2O_3 ratio of > 8 , and little Al_2O_3 , a composition which does make them highly chemically resistant but leads to disadvantageously high working points. These glasses, which in some cases have levels of ZrO_2 (up to 3% by weight) and the ZrO_2 -containing borosilicate glasses described in DD 301 821 A7 likewise have low thermal expansions of at most $5.3 \times 10^{-6}/K$ and $5.2 \times 10^{-6}/K$ and, in particular on account of their ZrO_2 contents, are highly resistant to lyes, but relatively susceptible to crystallization.

The glasses described in DE 198 42 942 A1 and DE 195 36 708 C1, have very high chemicals stabilities, being classified as belonging to hydrolytic, acid and lye class 1. However, the abovementioned drawbacks also apply to these glasses, on account of their high levels of ZrO_2 .

Moreover, - in the glasses of the prior art, the problem of the evaporation of alkali metals described above during the hot further processing of preshaped glass bodies will continue to occur.

This problem is neither referred to nor solved in DE 33 10 846 A1, which describes BaO-free laboratory glasses.

10 It is an object of the invention to find a glass which satisfies high demands both with regard to the chemicals resistance, i.e. belongs to lye class 2 or better, to hydrolytic class 1 and to acid class 1, and 15 on workability and has little evaporation of alkali metals.

This object is achieved by the glass described in patent claim 1.

20 The glass according to the invention has an SiO₂ content of 70 to 77% by weight, preferably of 70.5 to 76.5% by weight of SiO₂. Higher levels would increase the working point excessively and reduce the 25 coefficient of thermal expansion too far. If the SiO₂ content is reduced further, in particular the resistance to acids would deteriorate. An SiO₂ content of < 75% by weight is particularly preferred.

30 The glass contains 6 to < 11.5% by weight, preferably 6.5 - < 11.5% by weight, particularly preferably at most 11% by weight of B₂O₃. B₂O₃ reduces the working temperature and the melting temperature while, at the same time, improving the hydrolytic stability. This is 35 because B₂O₃ bonds the alkali metal ions which are present in the glass more securely into the glass structure. While lower contents would not reduce the melting point sufficiently far and would lead to an

increase in the susceptibility to crystallization, higher contents would have an adverse effect on the acids resistance.

- 5 The glass according to the invention contains between 4 and 8.5% by weight, preferably up to 8% by weight, of Al_2O_3 . Like B_2O_3 , this component bonds the alkali metal ions more securely into the glass structure and has a positive effect on the resistance to crystallization.
- 10 At lower contents, the susceptibility to crystallization would rise accordingly and, in particular with high B_2O_3 contents, there would be an increased evaporation of alkali metals. Excessively high levels would make their presence felt in terms of
- 15 an increase in the working and melting points.

For the glasses according to the invention, it is essential for the levels of the individual alkali metal oxides to be within the following limits:

- 20 The glasses contain 4 - 9.5% by weight, preferably 4.5 - 9% by weight of Na_2O . They may contain up to 5% by weight of K_2O and up to 2% by weight, preferably up to 1.5% by weight of Li_2O . The sum of the alkali metal oxides is between 5 and 11% by weight, preferably between 5.5 and 10.5% by weight, particularly preferably between 7.5 and < 10.5% by weight. The alkali metal oxides reduce the working point of the glasses and are of crucial importance for setting the thermal expansion. Above the respective upper limits, the glasses would have excessively high coefficients of thermal expansion. Furthermore, excessively high levels of the components would have an adverse effect on the hydrolytic stability. Furthermore, for cost reasons, it
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- 35 is recommended to limit the use of K_2O and Li_2O to the maximum levels indicated. On the other hand, an insufficient level of alkali metal oxides would lead to glasses with a thermal expansion which is too low and

would increase the working and melting points. With a view to making the glasses resistant to crystallization, it is preferable to use at least two types of alkali metal oxides. Even small amounts of 5 Li_2O and/or K_2O in the range of a few tenths of % by weight allow diffusion of the components/assemblies involved in constructing the crystal phase toward the nucleus to be impeded and can therefore have a positive effect on the resistance to devitrification.

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As further components, the glass may contain the divalent oxide MgO in an amount of 0 - 2% by weight, preferably 0 - 1% by weight, and CaO in an amount of 0 - 2.5% by weight, preferably 0 - 2% by weight, 15 particularly 0 - < 2% weight. The sum of these two components is between 0 and 3% by weight, preferably between 0 and < 3% by weight. The two components vary the "length of the glass", i.e. the temperature range within which the glass can be worked. The different 20 strengths of network-modifying action of these components makes it possible, by exchanging these oxides for one another, to adapt the viscosity to the requirements of the particular production and working process. CaO and MgO reduce the working point and are 25 securely bonded into the glass structure. Surprisingly, it has been found that limiting the levels of CaO to small amounts reduces the evaporation of highly volatile sodium and potassium borate compounds during hot-forming. This is of particular importance for Al_2O_3 30 contents, while at high Al_2O_3 contents it is possible to tolerate relatively high levels of CaO . CaO improves the resistance to acids. The latter statement also applies to the component ZnO , which may be present in the glass in an amount of up to 1% by weight. 35 Furthermore, the glass may contain up to 1.5% by weight of SrO and up to 1.5% by weight of BaO , which increases the resistance to devitrification. The sum of these two components is between 0 and 2% by weight. The glass is

preferably free of SrO and BaO. Particularly for use as primary packaging material for pharmaceuticals, it is advantageous if the glass is free of BaO.

5 Furthermore, the glass may contain coloring components, preferably Fe_2O_3 , Cr_2O_3 , CaO , in each case in amounts of up to 1% by weight, while the sum of these components should also not exceed 1% by weight. The glass may also contain up to 3% by weight of TiO_2 . This component is 10 preferably used when, for special applications of the glass, damage to a fused glass/metal seal by UV radiation or the release of UV radiation is to be prevented.

15 The glass may contain up to < 0.5% by weight of ZrO_2 , resulting in an improvement in the resistance to lyes. The ZrO_2 content is limited to this low maximum level, since higher levels would excessively increase the working point. Secondly, high levels of ZrO_2 increase 20 the risk of flaws in the glass, since it is possible that particles of the relatively insoluble ZrO_2 raw material will remain unmelted and will pass into the product.

25 The glass may contain up to 1% by weight of CeO_2 . At low concentrations, CeO_2 acts as a refining agent, and at higher concentrations it prevents the glass from being discolored by radioactive radiation. Therefore, 30 seals produced using a CeO_2 -containing glass of this type still allows visual checks for any damage, such as cracks or corrosion to the conductor wire, even after exposure to radioactive radiation. Even higher concentrations of CeO_2 make the glass more expensive and lead to an undesirable inherent brownish-yellow 35 coloration. A CeO_2 content of between 0 and 0.3% by weight is preferred for applications in which the ability to avoid discoloration caused by radioactive radiation is not essential.

The glass may contain up to 0.5% by weight of F⁻. This reduces the viscosity of the melt, which accelerates refining.

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In addition to the components CeO₂ and fluorides, for example CaF₂, which have already been mentioned, the glass can be refined using standard refining agents, such as chlorides, for example NaCl, and/or sulfates, 10 for example Na₂SO₄ or BaSO₄, which the finished glass contains in standard amounts, i.e. depending on the amount and type of refining agent used, in amounts of from 0.005 to 1% by weight. If As₂O₃, Sb₂O₃ and BaSO₄ are not used, the glasses are, apart from inevitable 15 impurities, free of As₂O₃, Sb₂O₃ and BaO, which is advantageous in particular for use as primary packaging material for pharmaceuticals.

Examples

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Twelve Examples of glasses according to the invention (A) and three comparative Examples (C) were melted from standard raw materials.

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The glasses were produced in the following way: the raw materials were weighed out and thoroughly mixed. The glass mix was melted at approx. 1600°C and then poured into steel molds.

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Table 1 shows the respective composition (in % by weight, based on oxide), the coefficient of thermal expansion $\alpha_{20/300}$ [10⁻⁶/K], the transformation temperature T_g [°C], the softening point E_w, the working point V_A [°C], which corresponds to the temperature at a viscosity of 10⁴ dPas, the temperature at the viscosity 10³ dPas L₃ [°C] and the difference L₃ - V_A [K], the density [g/cm³] and the hydrolytic stability, the acid resistance and the lye resistance of the glasses.

The chemical resistances were determined in the following ways:

5 • the hydrolytic stability H in accordance with DIN ISO 719. The table in each case indicates the base equivalent of the acid consumption as $\mu\text{g Na}_2\text{O/g}$ of glass grit. The maximum value for a chemically highly resistant glass belonging to Hydrolytic Class 1 is 31 $\mu\text{g of Na}_2\text{O/g}$.

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15 • the acid resistance S in accordance with DIN 12116. The table in each case indicates the weight loss in mg/dm^2 . The maximum loss for an acid-resistant glass belonging to Acid Class 1 is 0.70 mg/dm^2 .

20 • the lye resistance L in accordance with DIN ISO 695. The table in each case indicates the weight loss in $\mu\text{g/dm}^2$. The maximum loss for a glass belonging to Lye Class 1 (weakly soluble in lyes) is 75 mg/dm^2 . The maximum loss for a glass belonging to Lye Class 2 (moderately soluble in lyes) is 175 mg/dm^2 .

25 The requirements, namely Class 1 for H and S and at least 2 for L are satisfied in the glasses according to the invention. They are therefore highly chemically resistant. In particular with regard to hydrolytic stability, which is especially important for pharmaceutical applications, they produce excellent results, with values which are extremely low within H = 1, namely base equivalents of $\leq 12 \mu\text{g of Na}_2\text{O/g}$.

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Their low working points V_A of at most 1180°C characterize their good and inexpensive workability.

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The glasses according to the invention are eminently suitable for all applications in which chemically highly resistant glasses are required, for example for

laboratory applications, for chemical installations, for example as tubes.

The glasses have a coefficient of thermal expansion $\alpha_{20/300}$ of between > 5.0 and $6.0 \times 10^{-6}/K$, and in a preferred form of at least $> 5.2 \times 10^{-6}/K$, and in a particularly preferred form of between > 5.3 and $5.9 \times 10^{-6}/K$, which can be varied in particular by means of the alkali metal content. Therefore, their linear expansion is well matched to that of Fe-Co-Ni alloys, e.g. Vacon[®] 11 ($\alpha_{20/300} = 5.4 \times 10^{-6}/K$), and to zirconium ($\alpha_{20/300} = 5.9 \times 10^{-6}/K$), and the glasses are suitable for fused glass/metal seals with these chemically highly resistant metals or alloys. In view of their own high chemicals resistance, they are therefore particularly suitable for fused glass/metal seals which are used in chemically corrosive environments, for example in the construction of chemical installations or reactors, or as pressure viewing glasses, glasses for viewing windows in steel pressure vessels in which chemically aggressive substances are also kept under pressure.

The glasses are suitable for sealing and soldering glasses and as sheathing glass for glass fibers.

Table 1

Compositions (in % by weight, based on oxide) and properties of glasses according to the invention (A) and comparative glasses (C)

	A1	A2	A3	A4	A5	A6	A7	A8
SiO ₂	74.1	74.6	74.0	75.6	76.1	73.0	73.0	76.1
B ₂ O ₃	10.6	10.7	10.6	8.3	8.4	10.4	9.0	7.0
Al ₂ O ₃	5.7	5.8	5.7	6.3	5.7	5.6	6.9	6.9
Li ₂ O	0.2	1.0	-	0.15	-	0.2	0.7	1.0
Na ₂ O	8.0	6.5	8.4	8.3	8.45	5.0	7.0	5.0
K ₂ O	-	-	-	-	-	4.5	2.0	4.0
MgO	-	-	-	-	-	-	0.5	-
CaO	1.4	1.4	1.3	1.35	1.35	1.3	0.5	-
ZrO ₂	-	-	-	-	-	-	0.2	-
CeO ₂	-	-	-	-	-	-	0.2	-
$\alpha_{20/300}$ [10 ⁻⁶ /k]	5.31	5.05	5.35	5.39	5.33	5.55	5.84	5.68
Tg [°C]	562	530	574	562	585	556	545	530
Ew [°C]	787	767	805	783	807	811	753	774
V _A [°C]	1136	1129	1137	1167	1170	1146	1138	1175
L ₃ [°C]	n.d.	n.d.	1349	1397	n.d.	n.d.	n.d.	1415
L ₃ -V _A [k]	n.d.	n.d.	212	230	n.d.	n.d.	n.d.	240
p [g/cm ³]	2.350	2.340	2.360	2.361	2.360	2.360	2.362	2.353
H [μg Na ₂ O/g]	10	12	9	7	7	10	12	9
S [mg/ dm ²]	0.4	0.6	0.4	0.3	0.3	0.6	0.8	0.5
L [mg/ dm ²]	102	102	104	90	85	107	83	86

n.d. = not determined

Continuation of Table 1

	A9	A10	A11	A12	C1	C2	C3
SiO ₂	71.0	71.0	76.1	71.0	72.8	73.3	71.9
B ₂ O ₃	11.0	11.0	10.4	11.0	11.5	11.5	8.9
Al ₂ O ₃	8.0	8.0	4.0	8.0	3.5	3.5	7.0
Li ₂ O	0.5	-	-	1.0	-	1.0	1.3
Na ₂ O	5.0	8.5	5.0	8.5	5.5	8.5	5.5
K ₂ O	4.5	-	4.5	-	4.5	-	1.6
MgO	-	-	-	-	-	-	-
CaO	-	1.5	-	0.5	2.2	2.2	1.8
ZrO ₂	-	-	-	-	-	-	2.0
CeO ₂	-	-	-	-	-	-	-
α _{20/300} [10 ⁻⁶ /K]	5.68	5.42	5.34	5.90	5.73	5.97	5.42
Tg [°C]	531	579	568	533	568	540	540
Ew [°C]	758	754	793	715	769	791	765
V _A [°C]	1149	1169	1155	1071	1130	1125	1144
L3 [°C]	1384	1390	1365	1284	n.d.	n.d.	n.d.
L3-V _A [K]	235	231	210	213	n.d.	n.d.	n.d.
p [g/cm ³]	2.328	2.321	2.343	2.363	2.381	2.394	2.380
H [μg Na ₂ O/g]	11	8	8	12	n.d.	n.d.	10
S [mg/ dm ²]	n.d.	n.d.	0.6	n.d.	n.d.	0.6	0.6
L [mg/ dm ²]	135	133	105	118	n.d.	n.d.	62

n.d. = not determined

The glasses according to the invention have low temperature differences between L_3 , the temperature at viscosity 10^3 dPas, and V_A , the temperature at viscosity 10^4 dPas, namely less than 250 K. This is advantageous for the further processing of hot-formed glass products, since the evaporation of alkali metals is reduced. This is because, as thermogravimetric tests have shown, it is dependent not only on the working point V_A but also on the further viscosity profile toward lower viscosities.

Figure 1 shows, for 2 example glasses according to the invention (A3 and A4), the result of a thermogravimetric test. The figure plots the mass loss [%] against \log (viscosity [dPas]). When heated at a constant heating rate, the glass specimens, beyond approx. 1000 °C, represent a low mass loss which, as demonstrated by mass spectrometry and X-ray analyses carried out on the condensation products from the melting process, is attributable to the evaporation of alkali metal borates. The figure illustrates that a low temperature difference $L_3 - V_A$ is desirable with a view to minimizing the evaporation of alkali metals.

The advantages of the present invention are made even clearer by quantitative characterization of the alkali metal evaporation by means of spectrometry methods. An optical detection method of this type has a higher measurement sensitivity while using a simpler test arrangement which is less susceptible to faults. Time-dependent spectrometer measurements were carried out on a number of example and comparative glasses. The spectrometer measurements are carried out on heated, rotating cylindrical specimens with a diameter of approx. 4 mm, using a multichannel spectrometer Zeiss MMS1. Having been excited by a supply of heat from a gas burner, the alkali metal ions which escape from the glass emit light of a specific wavelength, inter alia

at approx. 589 nm (Na), 767 nm (K) and 670 nm (Li). The respective signals increase continuously as the test duration increases, approximately proportionally to the introduction of energy and also indicating a 5 correspondingly reduced viscosity of the specimens.

Taking account of the molar levels of the alkali metal oxides Na_2O , K_2O and Li_2O in the glass, a qualitative dependency of the intensities I at the same test times 10 is observed in the glasses throughout the entire period of the test, corresponding to I (K) > I (Na) > (Li), i.e. potassium borates evaporate more easily than sodium borates, while lithium borates are relatively difficult to evaporate out of heated borosilicate 15 glass.

Table 2 shows example spectrometer data for the glasses A8 - A12 and C1 - C2. For the compositions of these 20 glasses, refer to Table 1. All the numerical values given in Table 2 represent means from 7 measurements carried out on different specimens from the same casting. The intensities of the examples A8, A9 and A11 are given in relation to the intensity values of C1. The intensities of A10 and A12 and C3 were related to 25 C2. I (Li) of A8 and A9 is not given, since there is no reference value, as C1 is Li-free. I (Li) of A8 and A9 is, however, taken into account in I (total) of A8 and A9.

30 I (total) results from the formula I (total) = I (Na) + I (K) \times 0.65 + I (Li) \times 2.09.

This formula is used in the standard way to calculate 35 characteristic data for the surface resistances of ampoules and small bottles in accordance with ISO 4802-2. In this case, the alkali metals are determined by flame photometry and the result is given as equivalent Na_2O (ppm). The factors therefore

correspond to the molar weight ratios $\text{Na}_2\text{O}/\text{K}_2\text{O}$ and $\text{Na}_2\text{O}/\text{Li}_2\text{O}$.

In detail, Table 2 shows:

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$I(\text{Na})$; time 3.5 s = integral intensity of the sodium peak at test time 3.5 s $\cong 1200^\circ\text{C}$

$I(\text{Na})$; time corresponding to V_A = integral intensity of the sodium peak at a test time at which the temperature of the specimen (pyrometric measurement) corresponds to V_A

$I(\text{K})$; time 3.5 s = integral intensity of the potassium peak at test time 3.5 s $\cong 1200^\circ\text{C}$

$I(\text{K})$; time corresponding to V_A = integral intensity of the potassium peak at a test time at which the temperature of the specimen (pyrometric measurement) corresponds to V_A

$I(\text{Li})$ 3.5 s = integral intensity of the lithium peak at test time 3.5 s $\cong 1200^\circ\text{C}$

$I(Li)$; time corresponding to V_A = integral intensity of the lithium peak at a test time at which the temperature of the specimen (pyrometric measurement) corresponds to V_A

I (total); time 3.5 s calculated according to
 I (total) = I (Na) +
 I (K) × 0.65 + I (Li) × 2.09

I (total); time corresponding to V_A calculated according to
 I (total) = I (Na) +
 I (K) × 0.65 + I (Li) × 2.09

The data are relative intensities, in each case in relation to the intensity which is set at $I = 1.00$.

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Comparing the measurement data from Table 2 demonstrates that the glasses according to the invention have lower intensities than the corresponding comparative glasses. Since these measurements are carried out on reheated castings, this measurement method is eminently suitable for providing information about the evaporation of alkali metals, as occurs during hot further processing of preforms, e.g. the production of ampoules from glass tube.

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The glasses according to the invention therefore have a reduced evaporation of alkali metals and are consequently eminently suitable for the production of primary packaging materials for pharmaceuticals, for example ampoules.

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Table 2

Spectrometer data for Na (589 nm), potassium (767 nm) and Li (670 nm); relative intensities

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	A8	A9	A11	C1
I (Na); time 3.5 s	0.87	0.80	0.87	1.00
I (Na); time corresponding to V_A	0.94	0.84	0.93	1.00
I (K); time 3.5 s	0.78	0.76	0.89	1.00
I (K); time corresponding to V_A	0.89	0.81	0.97	1.00
I (Li); time 3.5 s			-	-
I (Li); time corresponding to V_A			-	-
I (total) time 3.5 s	0.87	0.81	0.88	1.00
I (total) time corresponding to V_A	0.96	0.85	0.95	1.00

	A10	A11	C2	C3
I (Na); time 3.5 s	0.82	0.90	1.00	
I (Na); time corresponding to V_A	0.96	0.92	1.00	
I (K); time 3.5 s	-	0.21	-	
I (K); time corresponding to V_A	-	0.21	-	
I (Li); time 3.5 s	-	0.98	1.00	
I (Li); time corresponding to V_A	-	1.18	1.00	
I (total) time 3.5 s	0.76	0.99	1.00	1.55
I (total) time corresponding to V_A	0.91	0.97	1.00	1.74